# Evolution of the conductivity of potassium-doped pentacene films

M. F. Craciun, S. Rogge, and A. F. Morpurgo

*Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands*

We have investigated the evolution of the temperature-dependent conductivity of electron-doped pentacene (PEN) thin films, in which the electron density is controlled by means of potassium (K) intercalation. We find that the conductivity is high and exhibit metallic temperature dependence in a broad range of concentrations up to approximately 1 K/PEN. At this value, charge transfer from potassium to PEN saturates, leaving the lowest unoccupied molecular orbital at half filling. This causes a sharp drop of the conductivity, concomitantly with a re-entrance into an insulating state. Our observations are consistent with the occurrence of a Mott-Hubbard insulating state driven by strong electron-electron interaction in agreement with theoretical predictions.

Pentacene (PEN) is a conjugated molecule very well-known in the field of plastic electronics for its use in high-mobility organic thin-film [1], whose electronic properties are being investigated in great depth. One aspect that has attracted particular attention is the possibility to control the electrical conductivity by means of chemical doping. Doping is achieved through the inclusion of iodine [2, 3, 4] and alkali atoms [5, 6, 7, 8], that intercalate in between the planes of the molecular films -as shown by many different structural studies [2, 3, 4, 5, 6, 7, 8, 9, 10]- and donate either holes (iodine) or electrons (alkali) to the molecules. For iodine doping [2, 3, 4] earlier, and very recently also for rubidium doping [9], it has been found that the conductivity of pentacene films can become large ($\approx 100$ S·cm$^{-1}$) and exhibit a metallic temperature dependence. However, very little is currently known about the doping dependence of the conductivity and the microscopic nature of electrical conduction in doped pentacene.

Here, we address these issues by investigating the evolution of the temperature-dependent conductivity of potassium-intercalated PEN thin films, with increasing doping concentration. We find that the conductivity is high and exhibit metallic temperature dependence for potassium concentrations between approximately 0.1 K/PEN and 1 K/PEN. When the amount of potassium is increased beyond 1 K/PEN, a sharp drop of the conductivity is observed, concomitantly with a re-entrance into an insulating state. The analysis of the experimental data show that at high doping the conductivity cannot be described in terms of independent electrons filling the molecular band originating from the lowest unoccupied molecular orbital (LUMO). Rather, our observations are consistent with the occurrence of a Mott-Hubbard insulating state driven by strong electron-electron interaction, in agreement with recent theoretical predictions [11].

Our experiments are carried out on pentacene thin films ($\sim 25$nm thick) thermally evaporated from a Knudsen cell on an H-terminated Si surface. The deposition of PEN films, their doping, and the temperature-dependent transport measurements are carried out *in-situ* in a single ultra-high (UHV) vacuum system with a base pres-

sure $< 5 \times 10^{-11}$ mbar. The substrate was kept at room temperature during the evaporation of pentacene. The film thickness was determined ex-situ using an atomic force microscope (AFM). Prior to the film deposition, as-purchased molecules were purified by means of physical vapor deposition in a temperature gradient in the presence of a stream of argon as described in ref. [19]. The substrates were prepared from a high resistive silicon-on-insulator (SOI) wafer, consisting of a top $2\mu$m silicon layer electrically insulated from the Si substrate by $1\mu$m-thick SiO$_2$ buried layer (see Fig.1B). The electrodes (Ti 10nm thick / Au 50nm thick) were deposited on SOI before loading the substrates in the UHV system. The H-terminated Si surface was obtained by etching the SOI surface in HF solution and rinsing in de-ionized water. The use of SOI enables the growth of highly ordered films, while minimizing the parallel conduction through the substrate. The high quality of these films is essential, as the worst structural quality of films deposited on insulating surfaces (e.g., glass) results in considerably poorer electrical properties. Doping is achieved by exposing the films to a constant flux of K atoms generated by a current-heated getter source. The potassium concentration is determined by means of an elemental analysis performed on pentacene films doped at several doping levels, using ex-situ Rutherford backscattering technique (RBS). As shown in Fig.1C, the ratio of K atoms to PEN molecules is increasing linearly with increasing the doping time, as expected.

The doping dependence of the conductivity (doping curve) of PEN films is shown in Fig.1A. Despite small differences in the doping curves of different samples (illustrated by the two curves in the figure), the overall trend is very similar for all the (more than 40) films measured. The conductivity rapidly increases with doping up to a value of $\sigma \sim 100 S/cm$, it remains high in a broad range of concentrations, and it eventually decreases to the level observed for the pristine material (over-doped state) for potassium concentrations higher than 1 K/PEN. We note that the observed suppression of the conductivity at high doping exclude the possibility that the observed conduction is due to experimental artifacts, such as, for instance, the formation of a potassium layer on top of the pentacene film.
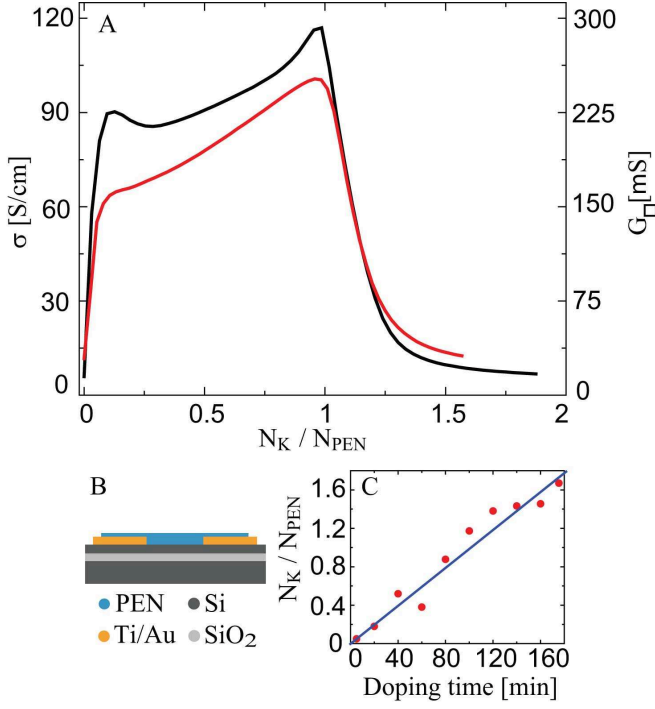
FIG. 1: (A) Conductivity measured at room temperature as a function of potassium concentration for two PEN films. (B) Schematic layout (side view) of a pentacene film on a SOI substrate with prefabricated electrodes (not to scale). (C) Doping calibration performed by means of RBS.
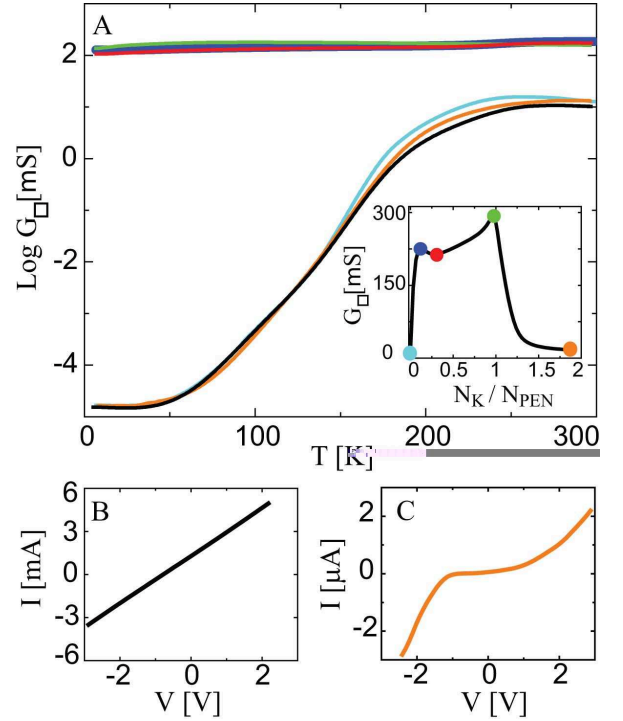


FIG. 2: (A) Temperature dependence of the square conductance of pentacene films measured for the undoped, the highly conductive and the over-doped states. The colored dots in the inset of (A) indicate the doping level at which the temperature dependence curves of the corresponding colors have been measured. The temperature dependence of the SOI substrate (in black) is also shown. Low temperature (5K) measurements of the I-V characteristics of films in the highly conducting and the over-doped states are shown in (B) and (C), respectively.

To investigate the nature of electrical conduction, we have measured the temperature dependence of the conductivity at different doping levels (Fig.2). For undoped materials, the conductivity of the PEN film is very low, the measurements are dominated by transport through the 2 $\mu$m thick Si layer of the SOI substrate. The observed temperature dependence is insulating, as expected. When the films are doped into the highly conductive state (i.e. for K/PEN in between 0.1 and 1) the conductance of the doped films remains high when lowering the temperature, down to the lowest temperature reached in the experiments ($\sim$ 5 K). This demonstrates the occurrence of metallic conduction. In the over-doped state (for $K/PEN > 1$) the conductance is again dominated by the substrate and decreases very rapidly with decreasing temperature, i.e. over-doped films are insulating. To further verify the metallic nature of the different doping states, we have measured the low-temperature (5K) I-V characteristics at different doping levels. At potassium concentrations between 0.1 and 1 K/PEN, the films exhibit linear I-V characteristics (Fig.2B), as expected for a metal, whereas over-doped films show a strong non-linearity and virtually no current when the applied bias is less than 1 V (Fig.2C), signaling a non conducting state.

Earlier investigations [5, 6, 7] had failed to find a metallic behavior in alkali-doped pentacene films. The difference between our and early results originates from the high quality of the films that can be achieved on a hydrogen-terminated Si surface. To clarify this important technical point, Fig.3A illustrates the doping dependence of films deposited onto glass substrates.
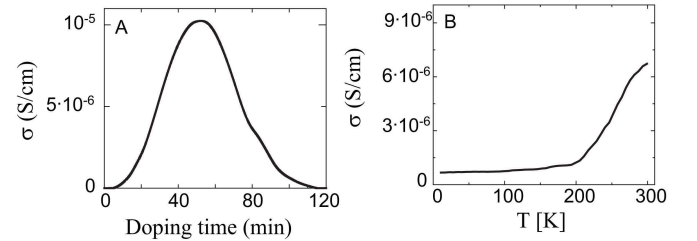


FIG. 3: (A) Conductivity measured at room temperature as a function of doping time for films of pentacene deposited on glass. (B) Temperature dependence of the conductivity for pentacene films grown on glass measured into the optimally doped state.

The maximum conductivity (optimally doped state)

is several orders of magnitude lower than the conductivity measured for films deposited on a Si surface. In addition, the conductivity of potassium-doped films on glass substrates was always observed to decrease rapidly with lowering temperature, i.e. the films are insulating (see Fig.3B). Both the magnitude and the temperature dependence of the conductivity that we measured on glass substrates compares well to results reported in earlier work.

We attribute the difference in the electrical behavior observed for films deposited on Si and glass substrates to the difference in film morphology, which we have analyzed using an atomic force microscope. Figure 4 shows AFM images of two pentacene films of similar thickness deposited on the hydrogen terminated Si (Fig.4A) and on the glass surface (Fig.4B). It is apparent that very different morphologies are observed for the two substrates. PEN films deposited on Si surfaces exhibit large crystalline grains with a common relative orientation and only relatively small fluctuations in height. On glass, on the contrary, the grains are much smaller, randomly oriented and they exhibit much larger height fluctuations.
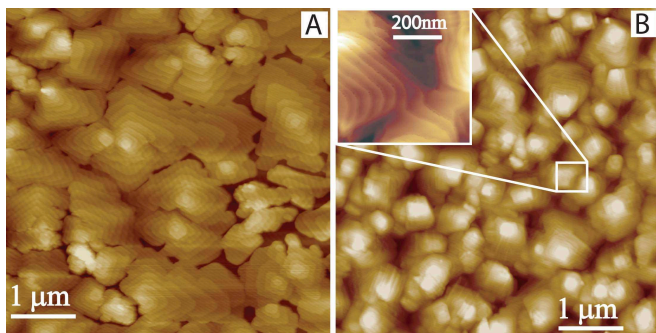


FIG. 4: AFM images of pentacene films grown on H-terminated Si (A) and on glass (B). The inset of (B) shows the layered structure of the grains for the films deposited on glass.

Our findings are consistent with the studies of Ruiz et al, which had shown that the growth and morphology of pentacene films is strongly influenced by the surface termination of the substrate [18]. Specifically, for pentacene films grown on $SiO_2$, a high density of nucleation centers was observed leading to the growth of small islands and to a high concentration of grain boundaries. On the hydrogen terminated silicon surface, on the contrary, a much smaller density of nucleation centers was observed resulting in significantly larger islands and in a reduced density of grain boundaries. The critical influence of the film morphology on the electrical characteristics of electron-doped pentacene films is further supported by very recent experiments [9] by Kanedo et al. in which metallic conduction in rubidium-doped films deposited on glass was observed

after performing a high-temperature annealing on the doped films, resulting in an improved morphological quality.

The most striking aspect of our observations, that had never been previously reported, is the sharp suppression occurring as the doping level is increased above 1 K/PEN. In this respect, PEN behaves differently from $C_{60}$ [12] and the metal phthalocyanines [13, 14], the only other molecular compounds in which a metallic state has been induced by alkali intercalation. For these molecular systems, a much larger number of potassium atoms per molecule are needed to bring the film back into an insulating state (six for $C_{60}$ and four for the metal phthalocyanines). This observation is important, as it implies that the conductivity of pentacene at high doping cannot be described in terms of independent electrons filling the molecular band originating from the LUMO orbital. In fact, for independent electrons the conductivity at 1 K/PEN should be metallic -as 1K/PEN corresponds to a half filled band-and should remain metallic up to 2 K/PEN, when all the spin-degenerate state in the molecular band are completely filled. This is not what is observed, as the films already enter an insulating state at potassium concentration higher than 1.1 K/PEN.

Having excluded a picture founded on independent electrons, our data point to an interpretation based on the concept of Mott-Hubbard insulator [15]. For most molecular systems, the on-site Coulomb interaction U of two charge carriers residing on the same molecule is much larger than the bandwidth W. In such a regime, transport of electrons is blocked at half filling because electron motion necessarily requires double occupation of molecular sites that are not energetically accessible. When this happens, the system is insulating due to strong-correlations induced by electron-electron interaction. For the oligoacenes (anthracene, tetracene, and pentacene) and the olithophenes, recent *ab-initio* calculations [11] show that U is always much larger than W. In particular, for pentacene $W = 0.6eV$ and $U = 1.4eV$. This corresponds to a U/W ratio of 2.3, for which a Mott-Hubbard insulating state is indeed expected and can therefore explain the transition to an insulating state observed in the data of Fig. 1A.

This interpretation implies that the charge transfer from the potassium atoms to the PEN molecules saturates at concentrations higher than 1 K/PEN, since otherwise a metallic conductivity should reappear when potassium concentration is increased well beyond 1 K/PEN. Such a conclusion is consistent with existing studies of charge transfer from alkali atoms to pentacene [16, 17] in a solid state matrix, in which only monoionic and no doubly charged states have been observed. Thus at potassium concentrations higher than 1 K/PEN the electron concentration in the films remains fixed at one electron per molecule, corresponding to a half-filled band. In this scenario, the width of the decay in conductivity observed for $K/PEN > 1$ (Fig.1A) is determined by the

inhomogeneity of the potassium concentration that, from our RBS measurements (Fig.1C), is estimated to be at the 20 % level. These considerations make clear that the saturation of charge transfer is essential for the observation of the Mott-Hubbard state on the conductivity of non-stoichiometrically doped films. In fact, as an insulating behavior due to Mott-Hubbard physics is only visible in a narrow range of doping close to one electron per molecule, the inhomogeneity in electron concentration present in the absence of charge transfer saturation would prevent its observation.

In conclusion, we have shown that in potassium-doped pentacene a metallic state occurs in a broad range of concentrations up to approximately 1 K/PEN. At this value, charge transfer from potassium to PEN saturates, leaving the films at half filling. This causes an insulating temperature dependence of the conductivity that we attribute to a Mott-Hubbard insulating state recently predicted from *ab-initio* calculations [11].

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